

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 096 556 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
02.05.2001 Bulletin 2001/18

(51) Int. Cl.<sup>7</sup>: **H01L 21/321**, C09G 1/00,  
C09K 13/00, B24B 37/00

(21) Application number: **99307999.5**

(22) Date of filing: **11.10.1999**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(71) Applicant:  
**International Business Machines  
Corporation**  
**Armonk, N.Y. 10504 (US)**

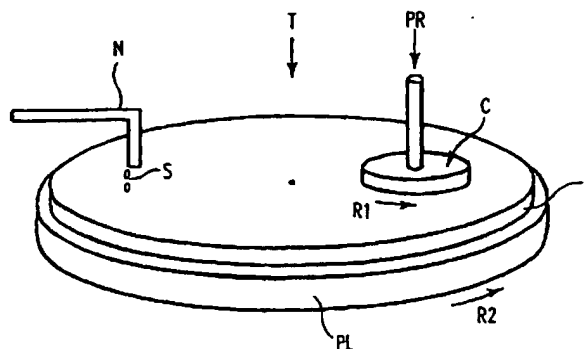
(72) Inventors:  
• **Brusic, Vlasta**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Edelstein, Daniel C.**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Fenney, Paul M.**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Guthrie, William**  
**Winchester, Hampshire SO21 2JN (GB)**

• **Jaso, Mark**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Kaufman, Frank B.**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Lustig, Naftali**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Roper, Peter**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Rodbell, Kenneth**  
**Winchester, Hampshire SO21 2JN (GB)**  
• **Thompson, David B.**  
**Winchester, Hampshire SO21 2JN (GB)**

(74) Representative:  
**Ling, Christopher John**  
**IBM United Kingdom Limited,**  
**Intellectual Property Department,**  
**Hursley Park**  
**Winchester, Hampshire SO21 2JN (GB)**

(54) **Chemical-mechanical planarisation of copper**

(57) Copper or a copper alloy is removed by chemical-mechanical planarisation (CMP) in a slurry of an oxidizer, an oxidation inhibitor, and an additive that appreciably regulates copper complexing with the oxidation inhibitor.



**FIG. 2**

**EP 1 096 556 A1**

## Description

### Field of the Invention

[0001] The present invention relates generally to integrated circuit metallisation, and more particularly to a method of planarising copper wiring.

### Background of the Invention

[0002] In the field of integrated circuit manufacturing, it is well known that significant density advantages result from forming planar metallisation patterns (where the metallisation patterns interconnect one or more transistors, capacitors, resistors, and other semiconductor electronic components formed on a wafer). One of the significant trends in the industry is to produce such planar metallisation patterns using so-called "chemical-mechanical polish" (or "chem-mech polish" or "CMP") techniques. In CMP, the frontside of the wafer is held against a rotating polish wheel, and a chemical slurry is introduced that facilitates the removal of one or more metal layers on the wafer through a combination of chemical reaction and physical abrasion. See for example USP 4,944,836, issued July 31, 1990 to Beyer et al. and assigned to the assignee of the present invention (a CMP method of planarising metal relative to surrounding passivation, or planarising passivation relative to metallurgy).

[0003] In addition to the general advantages afforded by CMP, particular density advantages result from forming an integrated metallurgy in pre-planarised passivation. That is, as shown in USP 4,789,648, issued December 6, 1988 to Chow et al. and assigned to the assignee of the present invention (hereinafter the "Chow patent"), integrated metallurgy (that is, a single layer of metal that includes both a vertical portion that extends down to underlying layers on a wafer to contact conductive structures formed thereon, and horizontal portions that provide electrical interconnection) can be formed by depositing and defining apertures through two passivation layers that are planarised by CMP, then depositing metal over the entire structure and polishing away portions of the metal that extend above the planarised passivation layers. Normally, the horizontal and vertical portions of the metallurgy are formed using two layers of metal; the Chow patent maximizes conductivity by eliminating the interlayer interface that normally exists between the horizontal and vertical portions of the metallurgy structure.

[0004] In the prior art, it is well known to utilize aluminum alloys or tungsten as the metallurgy for integrated circuits. However, the conductivity characteristics of these materials may not be sufficient as the minimum on-chip dimensions decrease below 0.25  $\mu\text{m}$ . These metallurgies are typically deposited on the wafer utilizing chemical vapour deposition and other deposition techniques. As interconnect dimensions are reduced

the aspect ratio (that is, the ratio of height relative to width) of vias, or openings, formed through interlevel dielectrics increases, leading to voids in metals deposited utilizing directional techniques. In addition, at smaller geometries metal lines become more susceptible to electromigration-induced faults. Thus, a recent development in the art has been the development of copper metallurgies. Copper has low resistivity, high electromigration resistance, and can be deposited by electroplating techniques that greatly reduce void formation. However, because copper is a soft metal without a highly protective native oxide, and cannot be easily patterned using standard reactive ion etching techniques, it presents unique challenges, particularly in the area of CMP.

[0005] Various slurries for CMP of copper (and/or barrier materials for copper) have been proposed in the prior art. These techniques include the following:

- 1) nitric acid, a polymer, a surfactant, and sulfuric or sulfonic acid for removing copper from printed circuit boards in a non-CMP process (USP 4,632,727, to Nelson and assigned to Psi Star);
- 2) iron-ammonia-EDTA (USP 4,954,142, to Patrick, et al. and assigned to the assignee of the present invention);
- 3) water, a solid abrasive, and one of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{AgNO}_3$  (USP 5,225,034 and divisional 5,534,490 to Yu et al. and assigned to Micron Technology);
- 4) an oxidizing agent and a silica abrasive, the slurry having a pH between 2 and 4, to polish tungsten, copper, titanium nitride, or tungsten silicide (USP 5,340,370 and divisional 5,516,346, to Cadieu et al. and assigned to Intel);
- 5) ammonium persulfate/KOH with a pH of 10 ("Alkaline Formulation for Chemical Mechanical Polishing of Copper Utilizing Azole Passivation", IBM Technical Disclosure Bulletin, Vol. 37, No. 10, Oct 1994 Pg. 187);
- 6) silica or alumina grains, aminoacetic acid, and hydrogen peroxide (European Patent Application 94119785.7, published 6/28/95, based on JP 313406/93);
- 7) colloidal silica, sodium chlorite, and deionized water (USP 5,451,551, issued September 5 1995 to Krishnan et al.);
- 8) an oxidizing agent, a surfactant, and deionized water, with a uniform dispersion of alumina particulates that have an aggregate size distribution of less than about one micron and an average diameter

less than approximately 0.4 microns (USP 5,527,423, issued June 18, 1996 to Neville et al and assigned to Cabot Inc.);

9) ferric nitrate, BTA, poly(ethylene glycol) and alumina particulates ("Chemical-Mechanical Polishing of Copper In Acidic Media," Luo et al., 1996 CMP-MIC Conference, Feb 22-23 1996, pp. 145-51);

10) use of alumina particulates in a first CMP slurry to polish the bulk metal (tungsten or copper), followed by use of silica particulates in a second CMP slurry to polish an underlayer of Ti/TiN (USP 5,676,587, issued October 14, 1997 to Landers et al. and assigned to the assignee of the present invention); and

11) Silica, glycine, and BTA (USP 5,770,095 to Sasaki et al., and assigned to Toshiba Corp.).

**[0006]** In general, the prior art set forth above deals with polishing of copper (in some cases with barrier materials) in conventional metal line or stud via applications. However, when polishing metal as shown in the Chow patent, particular challenges are presented that must be addressed in the CMP process.

#### Disclosure of the Invention

**[0007]** In the invention, copper is removed by CMP in a slurry that comprises an oxidizer, an oxidation inhibitor, and an additive that appreciably regulates copper complexing with the oxidation inhibitor, resulting in a high removal rate of copper without appreciable removal of the underlying metallic and dielectric layers or copper corrosion, and with minimal loss of copper in patterned interconnects.

#### Brief Description of the Drawings

**[0008]** The invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Fig. 1 is a cross sectional view of a substrate with a layer of copper thereon undergoing the CMP process of the invention; and

Fig. 2 is a schematic perspective view of the CMP tool for carrying out the process of the invention.

#### Detailed Description of the Invention

**[0009]** As shown in Fig. 1 of the present application, oxide 10 has narrow openings 12, and wide openings 14 that define the metal lines. Each opening is filled with liner 20 and copper 22. In the invention, the portions of the metal layer 22 (shown in dashed lines) formed

above the upper surface of the liner 20 are removed by CMP, utilizing the polishing slurry of the invention, resulting in the final upper surface 22A.

**[0010]** During this operation, four goals are to be achieved: high chemical mechanical removal rate of copper 22; a low removal rate of the liner material 20; low removal rate of the underlying dielectric 10; and prevention of copper corrosion. Clearly, one goal is to maximize the removal rate of the copper, because the faster the polish process is, the more wafers can be processed per unit time, and the lower the overall semiconductor manufacturing cost. The second goal, minimizing the removal rate of the liner 20 during the copper CMP, step provides for a good polish stop and leads to minimal loss of copper in the trenches 14. This loss of metal is typically referred to as "dishing," and is shown schematically in Fig. 1. As to the third goal, since as a practical matter there could be some loss of liner, especially at corners of trenches 14, one wants to minimize the removal rate of the exposed dielectric layer 10. Excess removal of the underlying dielectric introduces non-planarity in the final surface which can lead to difficulties in subsequent process steps. Finally, since copper is highly corrodible, we need to ensure that any corrosive aspects of the removal process are minimized. These four goals of the copper CMP process (high removal rate of copper, without appreciable removal of the underlying liner and dielectric, and without appreciable corrosion) can often be incompatible. For example, in the prior art removal rate of the bulk metal is often sacrificed in order to prevent excessive liner removal. Higher removal rates of the bulk metal are achieved at the expense of excess dishing of patterns or corrosion of the copper.

**[0011]** In the invention as shown in Fig. 1, the liner 20 is on the order of 40 nm thick, and is comprised of tantalum. Alternatives include other tantalum alloys such as tantalum nitride, as well as other refractory metals and refractory metal alloys such as tungsten, chromium, and titanium/titanium nitride. A Ta-based barrier layer appears to provide the best combination of (a) promoting adhesion of copper to the oxide layer 10, (b) preventing diffusion of copper, which can have adverse electrical effects on the underlying silicon circuitry, and (c) providing rate selectivity to copper during the CMP process. Then the copper 22 is deposited onto the wafer, to a thickness (measured from the upper surface of oxide layer 10 to the upper surface of the copper layer) of approximately one micron. The copper layer can be formed using any deposition process that adequately fills the trenches in oxide layer 10 without the formation of voids.

**[0012]** The copper layer is then removed via CMP to remove portions of these metal layers that overlay the upper surface of the passivation layer, so as to form a planar surface. In practice, as shown in Fig. 2, the workpiece of Fig. 1 is placed within a carrier C of a CMP tool T. Any one of a number of known CMP tools, including

those available from IPEC Corp. and Strasbaugh Corp. could be used to carry out the present CMP operation. The CMP tool T has a rotating polish wheel (or platen) PL on which is mounted a polish pad P. The CMP slurry of the invention is applied onto the polish pad P via nozzle N, and the carrier C brings the wafer into contact with the polish pad P. In practice, the carrier C spins in a direction R1 complementary to that of the polish wheel R2. In the operation described below, typically the polish wheel rotates at a speed of approximately 40-100 revolutions per minute (RPM), and the wafer holder spins at a speed of approximately 20-100 RPM. Further, the wafer holder applies pressure PR to force the carrier C carrying the wafer against the polish pad P. Urethane pads such as the IC1000 from Rodel, foam pads such as the Politec from Rodel, and other pad types can also be used with the slurry, but the inventors found that non-woven pads such as those available from Freudenberg or Thomas West Inc. optimize the overall results in this application. In the operation described below, the applied pressure PR is approximately 3-6 pounds per square inch (PSI) (20.7-41.4 kPa). In practice, these three variables (spin speed of the wafer holder, rotation speed of the polish pad, pressure) are interrelated, and can and do vary as a function of e.g. the hardness and thickness of the layer to be polished.

**[0013]** In the slurry of the invention, solids such as alumina particulates having an aggregate diameter at or below approximately 0.3 microns are used to enhance the physical abrasion in the reaction while minimizing excessive scratching or other surface damage. The slurry includes the following components:

1) an etchant that promotes copper oxidation, such as ferric nitrate and compounds thereof, hydrogen peroxide, potassium iodate, manganese oxide, ammonium hydroxide, ammonium persulphate, potassium persulphate, ammonium persulphate/sulfuric acid, potassium persulphate/sulfuric acid; ferric chloride/hydrochloric acid, chromic acid, chromic acid/hydrochloric acid, potassium bichromate/sulfuric acid, and stearic acid Fe(III) salts;

2) an inhibitor that prevents copper dissolution by reacting with the copper surface, such as various benzotriazole compounds sold under the trade-name "BTA" (e.g. 1-H benzotriazole, 1-OH benzotriazole, 1-CH<sub>3</sub> benzotriazole, 5-CH<sub>3</sub> benzotriazole, benzimidazole, 2 OH, 2-methyl-benzimidazole, 5-Cl benzotriazole); and

3) an additive consisting of a mixture of sodium salts of sulfated fatty alcohols that competes with BTA for Cu reaction sites to slow down Cu-BTA film growth, and acts as a wetting agent, as will be described in more detail below.

**[0014]** Before describing the process in detail, the

chemical reactions to be optimized will be generally explored. In the present invention, CMP of copper generally involves a steady state process whereby a few monolayers of a Cu-BTA thin film are formed during the exposure of copper to one of the oxidizers and inhibitors listed in (1&2) above. (The Cu-BTA film is on the order of 14 angstroms (1.4 nm) thick when ferric nitrate is used as an oxidizer and benzotriazole is the inhibitor). This Cu-BTA film, which prevents rapid uncontrolled dissolution of copper, is then removed by physical abrasion (i.e. by the solid particulates in the CMP slurry). As the first monolayers are removed, the exposed copper goes through the above-described reaction to form new Cu-BTA monolayers. In terms of planarisation, this process is inherently faster on higher portions of the Cu layer, because the polishing pad of the CMP tool imparts a greater pressure against such higher portions, promoting the physical abrasion portion of the reaction; in the lower portions of the Cu layer, there will be less physical abrasion, hence the reaction proceeds slower until such time as the upper surface of the Cu layer is planar (and hence is subjected to equal pressure from the polish pad). This cycle of abrasion/dissolution/passivation continues until the portions of the tantalum layer 20 on the upper surface of passivation 10 are exposed. The above-described cycle must be optimized to occur at the right rate. If the Cu-BTA reaction rate is high and a thick Cu-BTA layer is formed, the CMP removal rate decreases. In the case of a very slow reaction rate one runs the risk of corroding (uncontrolled dissolution) the copper interconnects. For abrading the Cu-BTA an aqueous colloidal suspension of alumina (Al<sub>2</sub>O<sub>3</sub>) is used. The use of a colloidal alumina with small particle size (as well as a nonwoven polish pad, as discussed below) was found to reduce scratching of the soft copper interconnects. Maintaining the slurry at low pH (on the order of 1.2-2.5) is done in order to enhance the removal rate of copper metal relative the underlying dielectric.

**[0015]** The inventors found that an additive, Duponol SP, a DuPont Company trade name for a mixture of sodium salts of sulfated fatty alcohols, was essential to enhancing the Cu slurry performance. Duponol SP is also known as Supralate SP from Witco Corporation, and Empimin LV33/A from Albright and Wilson Americas Inc. While the prior art utilizes surfactants to promote CMP slurry colloidal suspension, in the present invention the additive is used to enhance the CMP removal rates of copper. In the present formulation the slurry is maintained in suspension through mechanical stirring rather than by surfactant/alumina interactions. The surfactant disclosed here is an anionic surfactant of a considerably shorter chain length and lower molecular weight than the one used for example in the aforesaid Luo et al. article. The Luo et al. article teaches use of a nonionic surfactant, poly (ethylene glycol), having a molecular weight on the order of 1 Million, in order to promote slurry suspension by steric repulsion. The use

of a lower molecular weight poly(ethylene glycol) (MW=10,000) was found by Luo et al. to be ineffective in maintaining the slurry suspension.

**[0016]** When the present inventors used a Duponol-free, alumina/BTA/ferric nitrate slurry, the abrasive remained in suspension, but the Cu CMP removal rate was less than 50 nm/minute; it was only after adding Duponol SP, that the CMP removal rate rose to approximately 300nm/minute, which is beneficial for efficient semiconductor manufacturing. The present inventors believe that Duponol SP competes with BTA for adsorption sites on the copper surface, thus limiting the overall thickness of the copper-BTA surface layer, leading to the observed increase in CMP removal rates. In general, the Duponol SP serves to appreciably regulate the Cu-BTA complexing reaction, such that it occurs at the right rate to maximize the overall rate of Cu polishing while retarding corrosion. It is also noted that Duponol SP, because of its relatively low molecular weight, is very effective in reducing solution surface tension. When included in the copper slurry it enhances the wetting of the copper surface by the slurry/polish pad system which further enhances the polishing rate.

**[0017]** Duponol is described in the Merck Index (Eleventh Edition, S. Budavari, Ed. Publ. Merck & Co. Inc., Rahway, N.J., p. 683 (1989)) as a Gardinol type detergent mixture of sodium salts of sulfated fatty alcohols made by reducing the mixed fatty acids of coconut oil or cottonseed oil and of fish oils. As such, it has a distribution of hydrocarbon chain length ( $C_8$ - $C_{18}$ ) with the 8-atom carbon chain length being the main component in the case of Duponol SP. Pure sodium octyl sulfate,  $(CH_3)(CH_2)_7OSO_3Na$ , was also found to enhance the Cu CMP removal rate, albeit at higher concentrations than those required for Duponol SP. It is noted that the pure alkyl sulfates are considerably more expensive than their "natural" counterparts and thus of less practical value in a manufacturing environment. Sodium octyl sulfates are characterized by a relatively high critical micelle concentration ( $CMC=1.4 \times 10^{-1}$  M at 40°C in  $H_2O$ ), where CMC is the concentration at which colloid clusters of agglomerated surfactant molecules (micelles) start to form. The high CMC implies that a higher concentration of monomers can reach the copper/polishing pad interface before the onset of micelle formation, and thus can better regulate the Cu-BTA film formation. Also, since it is the monomeric form which contributes to reduction of interfacial tension and improved wetting, a high CMC surfactant is desirable. The Duponol concentrations used in the present slurry are estimated to be at or below the CMC, such that an appreciable amount of micelles are not formed.

**[0018]** Based on the foregoing, the inventors believe that in addition to Duponol SP and pure sodium octyl sulfate, other fatty alcohol sulfate surfactants would work that have a relatively low molecular weight (less than approximately 350) and have a relatively high CMC. Some examples include sodium octyl sulfate and

longer chain derivatives, sodium octyl sulfonate and longer chain derivatives, and Duponol WN which is a mixture of sodium octyl and decyl sulfate. Duponol WN is also known as Supralate WN from Witco Corp. or Empicol LB33/A from Albright and Wilson Americas, Inc.

**[0019]** In addition, the inventors found that this slurry did not appreciably remove the underlying tantalum layer 20 or the oxide 10. At Cu removal rates on the order of 300nm/minute, the above-described slurry also resulted in a removal rate ratio on the order of 100:1 to the underlying liner, and ratios in excess of 100:1 to the underlying oxide. Even at high alumina concentrations (3% solids), copper CMP removal rate ratios above 50:1 to the above materials were observed. In particular, the inventors found that the use of colloidal alumina particulates greatly enhanced removal rate selectivity of copper to the tantalum liner. While other particulates (such as colloidal silica) abrade copper and the underlying tantalum based films non-selectively, as discussed above, the inventors found that the above slurry with alumina particulates does not appreciably attack tantalum.

**[0020]** The inventors have found that controlling temperature during the polish process is important to maximize copper removal rate while minimizing dishing. More specifically, the inventors have found that the temperature of the slurry increases as the polish proceeds, due to the frictional forces inherent in the polish process as well as the temperature-activated chemical components of the above-specified copper complexing reaction. The inventors have found that if the temperature rises above approximately 100 degrees F, dishing of patterned wide lines results, because the polishing pad softens and begins to deform while at the same time the chemical component/etching of the CMP process increases. In practice, this temperature control is achieved by utilizing a water-cooled polishing platen.

#### Example 1

**[0021]** A workpiece prepared as above was polished in a colloidal alumina dispersion having particulates on the order of 0.3 microns or less, available, for example, from Cabot Corporation and other suppliers. This grain size appears to provide the optimum tradeoff between enhanced Cu removal rates and low removal rate in the barrier film, while reducing scratching in the Ta film. The slurry included 18 litres deionized water (0.3% alumina), 1.2 grams/litre BTA, 22 grams/litre ferric nitrate, and 3ml/litre Duponol SP, such that the total slurry had a pH of approximately 1.5. The resulting removal rate was approximately 300 nm/minute, and the removal rate ratio was approximately 100:1 to the underlying Ta layer.

**Example 2**

[0022] A workpiece prepared as above was polished in a colloidal alumina dispersion having particulates on the order of 0.3 microns or less, as described above. The slurry included 18 litres deionized water. In a series of experiments,

1) The BTA, ferric nitrate, and Duponol SP concentrations were held constant, and the percent of alumina solids was varied between 0.1% and 3%, with no appreciable effect on Cu removal rate or Ta selectivity. Above approximately 3% solids the selectivity to Ta began to decrease, albeit by a relatively low amount. Based on these results the inventors speculate that selectivity would still be acceptable up to approximately 15% solids (0.3% is preferred to maximize selectivity while minimizing expense, since increased % solids increases the overall cost of the slurry);

2) The percent alumina solids, ferric nitrate, and Duponol SP concentrations were held constant, and the amount of BTA was varied between 0.1 grams/litre and 4 grams/litre. Below approximately 0.5 grams/litre Cu corrosion was present; between approximately 0.5 grams/litre and 3 grams/litre the Cu CMP rate was fairly uniform; and above approximately 3 grams/litre removal rate begins to decrease;

3) The percent alumina solids, BTA, and Duponol SP concentrations were held constant, and the ferric nitrate concentration was varied between 2 grams/litre and 40 grams/litre. Below approximately 2 grams/litre the Cu removal rate dropped off exponentially; above approximately 2 grams/litre the removal rate rose linearly; above approximately 25 grams/litre removal rate did not increase significantly; and

4) The percent alumina solids, BTA, and ferric nitrate concentrations were held constant, and the Duponol SP concentration was varied. Below approximately 3 ml/litre Cu CMP removal rate decreased; no appreciable change in etch rate was observed at higher Duponol SP concentrations.

[0023] In addition to pure copper, the present invention is applicable to copper alloys that would be polished in accordance with the reaction kinetics described above (e.g. copper with up to approximately 5% of various metals such as Al, Sn, In, Ti, Ag, Mo, Zr, Mg, Cr, Au, and Pb).

[0024] It is to be understood that the above and other modifications can be made to the preferred embodiment as set forth above without departing from the spirit and scope of the present invention. For exam-

ple, in Example 2 the relative concentrations of the main elements of the slurry were varied individually. The inventors note that the concentrations of some of the constituents are directly related to one another, such that if the percentage concentration of one constituent was changed the concentrations of the other related constituents would change proportionately. As a specific example, if the ferric nitrate concentration were to be dropped below 2 grams/litre, the BTA concentration could drop below the low end of the concentration range set forth in Example 2.

**Claims**

1. A CMP slurry for polishing a layer of copper or a copper alloy, comprising an etchant, an oxidation inhibitor, and an additive that appreciably regulates complexing between copper and the oxidation inhibitor.
2. A CMP slurry as claimed in claim 1, wherein the layer of copper or a copper alloy is on a liner layer, said slurry providing a first removal rate of said copper or copper alloy and a second removal rate of said liner layer, said first removal rate being at least fifty times greater than said second removal rate.
3. A slurry as claimed in Claim 1 or Claim 2, wherein said etchant is selected from the group consisting of ferric nitrate and compounds thereof, hydrogen peroxide, potassium iodate, manganese oxide, ammonium hydroxide, ammonium persulphate, potassium persulphate, ammonium persulphate/sulfuric acid, potassium persulphate/sulfuric acid, ferric chloride/hydrochloric acid, chromic acid, chromic acid/hydrochloric acid, potassium bichromate/sulfuric acid, and stearic acid Fe(III) salt.
4. A slurry as claimed in Claim 1 or Claim 2, wherein said oxidation inhibitor is selected from the group consisting of 1-H benzotriazole, 1-OH benzotriazole, 1-CH<sub>3</sub> benzotriazole, 5-CH<sub>3</sub> benzotriazole, benzimidazole, 2 OH, 2-methyl-benzimidazole, and 5-Cl benzotriazole.
5. A slurry as claimed in Claim 1 or Claim 2, wherein said additive is comprised of a sodium salt of a sulfated fatty alcohol.
6. A slurry as claimed in Claim 5, wherein said sodium salt of a sulfated fatty alcohol is selected from the group consisting of sodium octyl sulfate and longer chain derivatives, sodium octyl sulfonate and longer chain derivatives, Duponol SP, and Duponol WN.
7. A slurry as claimed in Claim 5, wherein said sodium salt does not form an appreciable amount of micelles.

8. A slurry as claimed in Claim 1 or Claim 2, further comprising colloidal alumina.
9. A slurry as claimed in Claim 8, wherein said colloidal alumina has particulates having a size less than approximately 0.3 microns. 5
10. A slurry as claimed in Claim 1 or Claim 2, wherein said slurry has a pH of approximately 1.2-2.5. 10
11. A process for polishing copper or a copper alloy in a CMP tool comprising a wafer carrier and a polish pad, the method comprising the steps of:
- placing a wafer having a layer of copper on its upper surface into said wafer carrier; 15
- applying a slurry comprising an etchant, an oxidation inhibitor, and a sulfated fatty acid surfactant to said polish pad, said surfactant having a molecular weight less than approximately 350 and appreciably regulating complexing between copper and said oxidation inhibitor; and 20
- polishing said wafer by bringing said layer of copper into contact with said polish pad. 25
12. A process as claimed in Claim 11, wherein said etchant comprises ferric nitrate.
13. A process as claimed in Claim 12, wherein said oxidation inhibitor is selected from the group consisting of 1-H benzotriazole, 1-OH benzotriazole, 1-CH<sub>3</sub> benzotriazole, 5-CH<sub>3</sub> benzotriazole, benzimidazole, 2 OH, 2-methyl-benzimidazole, and 5-Cl benzotriazole. 30 35
14. A process as claimed in Claim 11, wherein said surfactant comprises a sulfated fatty acid selected from the group consisting of sodium octyl sulfate and longer chain derivatives, sodium octyl sulfonate and longer chain derivatives, Duponol SP, and Duponol WN. 40
15. A process as claimed in Claim 11, wherein said polish pad comprises a nonwoven polish pad. 45
16. A process as claimed in Claim 15, wherein said polishing step is carried out at a temperature below that at which said nonwoven polish pad appreciably deforms. 50
17. A tool for carrying out CMP of copper or a copper alloy on top of a barrier layer disposed on a work-piece, comprising: 55
- a wafer carrier for holding the wafer;
- a polish pad that contacts the wafer in said wafer carrier during the CMP operation; and
- a slurry providing a first removal rate of said copper or copper alloy and a second removal rate of said barrier layer, said first removal rate being at least fifty times greater than said second removal rate, said slurry comprising an etchant, an oxidation inhibitor, and an additive that appreciably regulates complexing between copper and the oxidation inhibitor.
18. A tool as claimed in Claim 17, wherein said polish pad comprises a nonwoven polish pad.
19. A tool as claimed in Claim 17, wherein said slurry is at a temperature below approximately 100 degrees F during said CMP process.

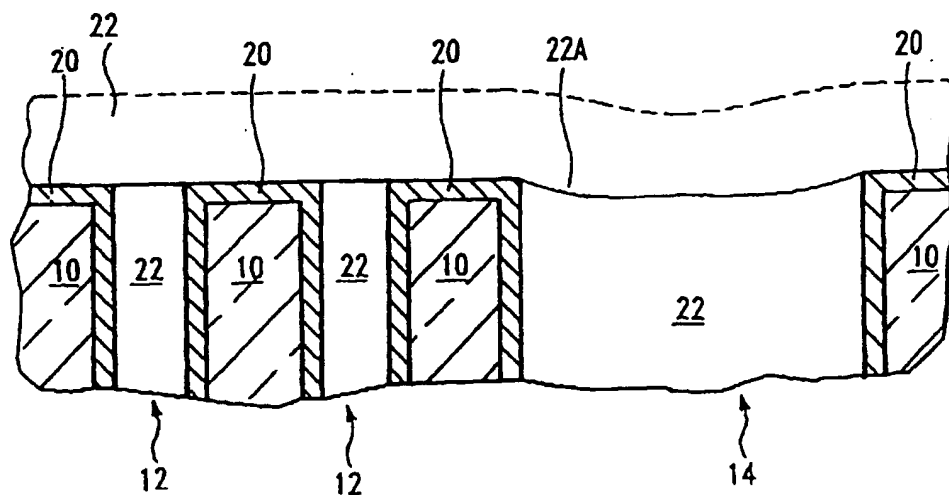


FIG. 1

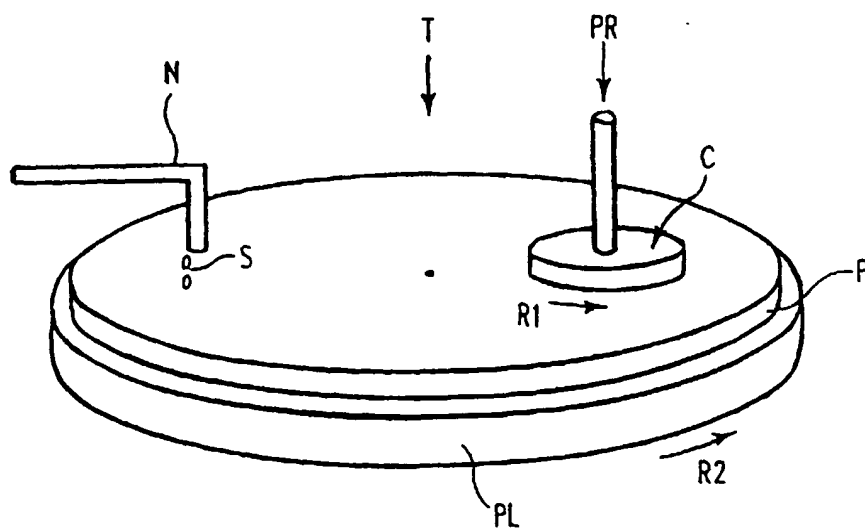


FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 7999

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |  |
|---|---|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim                                | CLASSIFICATION OF THE APPLICATION (Int.Cl.7)     |
| X   | EP 0 846 742 A (CABOT CORP)<br>10 June 1998 (1998-06-10)<br>* page 3, line 36 - page 6, line 2 *<br>* page 7, line 20 - line 34 *<br>---  | 1-8,10,<br>11,14                                 | H01L21/321<br>C09G1/00<br>C09K13/00<br>B24B37/00 |
| X   | WO 98 49723 A (WOOD THOMAS E ;HARDY L<br>CHARLES (US); KAISAKI DAVID A (US); KRANZ<br>H) 5 November 1998 (1998-11-05)<br>* page 6, line 19 - page 7, line 10 *<br>* page 28, line 20 - page 29, line 12 *   | 17-19  |  |
| A   | ---   | 1-4,9,<br>11-13,15                               |  |
| A   | US 5 897 375 A (GOMEZ JASON ET AL)<br>27 April 1999 (1999-04-27)<br>* column 1, line 45 - line 51 *<br>* column 4, line 54 - column 5, line 6 *<br>---  | 1-3,11,<br>12                                    |  |
| A   | EP 0 747 939 A (TOKYO SHIBAURA ELECTRIC<br>CO) 11 December 1996 (1996-12-11)<br><br>* abstract; claim 13 *<br>* figure 2 *  | 1,5,6,<br>11,14,<br>16,19                        | TECHNICAL FIELDS<br>SEARCHED (Int.Cl.7)          |
| A   | ---   |  | H01L   |
| A   | CARPIO R ET AL: "INITIAL STUDY ON COPPER<br>CMP SLURRY CHEMISTRIES"<br>THIN SOLID FILMS,CH,ELSEVIER-SEQUOIA S.A.<br>LAUSANNE,<br>vol. 266, no. 2,<br>1 October 1995 (1995-10-01), pages<br>238-244, XP000622864<br>ISSN: 0040-6090<br>* the whole document *<br>----- | 1-14   |  |
| The present search report has been drawn up for all claims  |   |  |  |
| Place of search<br>BERLIN   |   | Date of completion of the search<br>3 April 2000 | Examiner<br>Le Meur, M-A                         |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>.....<br/>&amp; : member of the same patent family, corresponding document</p> |   |  |  |

EPO FORM 1503 03/92 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 7999

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-04-2000

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| EP 0846742 A                              | 10-06-1998          | US 5954997 A               | 21-09-1999          |
|   |                     | AU 5373998 A               | 03-07-1998          |
|   |                     | JP 11021546 A              | 26-01-1999          |
|   |                     | WO 9826025 A               | 18-06-1998          |
| WO 9849723 A                              | 05-11-1998          | AU 7170698 A               | 24-11-1998          |
| US 5897375 A                              | 27-04-1999          | JP 11238709 A              | 31-08-1999          |
|   |                     | SG 67572 A                 | 21-09-1999          |
| EP 0747939 A                              | 11-12-1996          | JP 9055363 A               | 25-02-1997          |

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82